

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040065 A2

(51) International Patent Classification⁷: **C07B 37/02**,
C07C 41/06, B01J 31/24, C07F 9/50

(21) International Application Number: PCT/EP02/12381

(22) International Filing Date:
5 November 2002 (05.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/348,205 9 November 2001 (09.11.2001) US

(71) Applicant (for all designated States except US): **SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DRENT, Eit**

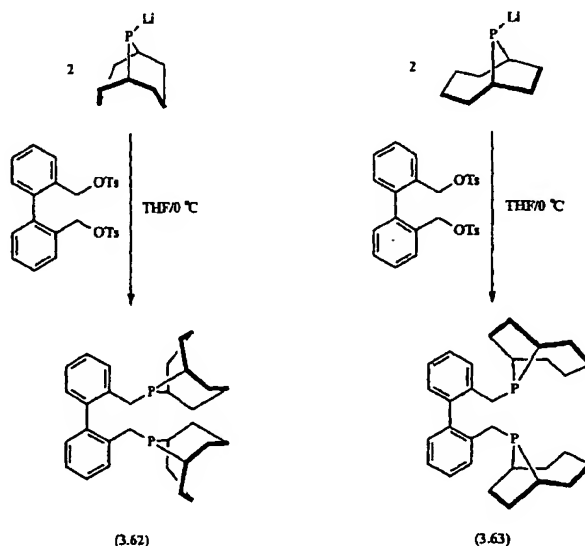
[NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **EBERHARD, Michael, Rolf** [DE/US]; 2545 McCarthy Mall, Honolulu, HI 96822 (US). **VAN DER MADE, Renata, Helena** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **PRINGLE, Paul, Gerard** [GB/GB]; Cantocks Close, Bristol, Avon BS8 1TS (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PROCESS FOR THE TELOMERIZATION OF A CONJUGATED DIENE, CATALYST AND BIDENTATE LIGAND USEFUL THEREIN



(57) Abstract: Process for the telomerization of a conjugated diene, wherein the conjugated diene is reacted with a compound containing an active hydrogen atom and having a formula R-H in the presence of a telomerization catalyst based on: (a) a source of group VIII metal, (b) a bidentate ligand wherein the bidentate ligand has the general Formula (I): $R^1R^2M^1-R-M^2R^3R^4$ wherein M^1 and M^2 are independently P, As or Sb; R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group; or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively; R represents a bivalent organic bridging group; and novel bidentate diphosphines which can be used in this process.

**Published:**

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

PROCESS FOR THE TELOMERIZATION OF A CONJUGATED DIENE,
CATALYST AND BIDENTATE LIGAND USEFUL THEREIN

The present invention relates to a process for the telomerization of a conjugated diene, and a catalyst and bidentate ligand that can be used in this process. In particular, this invention relates to a process for the telomerization of butadiene, and a catalyst and bidentate ligand that can be used in this process.

The telomerization of butadiene is known in the art from for example WO-A-9210450. WO-A-9210450 describes a telomerization reaction wherein 1,3-butadiene is reacted with a compound containing an active hydrogen atom and having a formula R-H in the presence of a telomerization catalyst to form a 1-substituted-2,7-octadiene of formula $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{R}$, in which R represent the residue of the compound containing an active hydrogen atom. WO-A-9210450 describes a wide range of telomerization catalysts. The telomerization catalyst disclosed in the example is a palladium acetylacetonate/triphenylphosphine based catalyst. With this telomerization catalyst the selectivity towards the desired linear 1-methoxy-2,7-octadiene telomerization product was 89.4%.

Although, in passing, the description mentions the possible use of diphosphine ligands, viz. bis(diphenylphosphine)ethane, no diphosphine ligand is disclosed in the examples.

The object of the present invention is to provide a process for the telomerization of a conjugated diene,

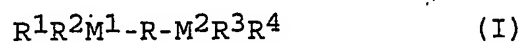
wherein the telomerization reaction can be carried out with an improved selectivity towards the linear telomerization product.

It has now been found that the telomerization of a conjugated diene can be carried out with a high selectivity towards the linear telomerization product in the presence of a specific catalyst system.

Accordingly, the present invention provides a process for the telomerization of a conjugated diene, wherein the conjugated diene is reacted with a compound containing an active hydrogen atom and having a formula R-H in the presence of a telomerization catalyst based on:

- (a) a source of group VIII metal,
- (b) a bidentate ligand

wherein the bidentate ligand has the general formula I



wherein M^1 and M^2 are independently P, As or Sb;

R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group;

or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of

which one is the M^1 or M^2 atom, respectively;

and R represents a bivalent organic bridging group.

The use of this specific catalyst system results in an improved selectivity towards the linear product whilst obtaining reaction rates well over 500 mol conjugated diene/mol group VIII metal/hour.

The conjugated diene preferably is a conjugated diene having from 4 to 20, more preferably from 4 to 8 carbon atoms per molecule. The conjugated diene can be

substituted or unsubstituted, and can contain a number of heteroatoms. Examples of conjugated dienes that can be used include 1,3-butadiene, isoprene 1,3-pentadiene, 1,3-hexadiene. Preferably the conjugated diene is unsubstituted and preferably the conjugated diene only contains carbon atoms. Most preferably, the conjugated diene is 1,3-butadiene.

In the telomerization process of 1,3-butadiene, 1-substituted-2,7-octadiene can be prepared. 1-substituted-2,7-octadiene can be useful in a process to prepare 1-octene containing substantially no branched olefinic C₈-isomers. Such a process is exemplified in WO-A-9210450. This invention therefore also relates to a process for the preparation of 1-octene, comprising:

- telomerization of 1,3-butadiene as described herein, to form 1-substituted-2,7-octadiene;
- hydrogenation of the 1-substituted-2,7-octadiene of step a) to form 1-substituted octane;
- decomposition of the 1-substituted octane of step b) to form 1-octene.

Step a) of this process can be carried out as described herein. Steps b) and c) are conveniently carried out as described in WO-A-9210450.

The conjugated diene used as a starting compound can contain small amounts of other saturated or unsaturated hydrocarbons. For example, a crude C₄ hydrocarbon mixture can be used as a feed for 1,3-butadiene. Such a crude C₄ mixture can contain, besides 1,3-butadiene other C₄-hydrocarbons such as butenes and butanes.

The active hydrogen-containing compound R-H can be any compound having a reactive hydrogen atom. Examples of such active hydrogen-containing compounds include

alkanols, hydroxy-aromatic compounds, carboxylic acids, ammonia, primary and secondary amines and water.

Preferred active hydrogen-containing compounds include water, alkanols and hydroxy-aromatic compounds.

Alkanols that can be used in the process of the invention include mono- or poly alkanols, which can be linear or branched and saturated or unsaturated. Preferred alkanols for the process of the invention are alkanols with from 1 to 20, more preferably with from 1 to 6 carbon atoms per molecule and alkanediols with from 2 to 20, more preferably from 2 to 6 carbon atoms per molecule. Suitable alkanols in the process of the invention include methanol, ethanol, ethanediol, propanol, 1,2-propanediol, 1,3-propanediol, iso-propanol, butanol, 1,2-butanediol, 1,4-butanediol, iso-butanol, tert.butanol, pentanol, hexanol, hexanediol, cyclohexanol, and cyclohexanediol. Of these, methanol, ethanol and phenol are preferred. Methanol and phenol are especially preferred.

Examples of hydroxy-aromatic compounds are aromatic compounds containing one or more rings such as phenol, benzylalcohol, cresols, xylenols, naphthol as well as polyhydric compounds such as resorcinol, hydroquinone and pyrocatechol. Also alkyl-, alkoxy- and/or halogen-substituted aromatic hydroxy compounds can be used.

Examples of carboxylic acids that can be used in the process of the invention include aliphatic carboxylic acids with up to about 20 carbon atoms. Preferred carboxylic acids are those having from 1 to 6 carbon atoms such as e.g. acetic acid, propionic acid, butyric acid. Examples of suitable aromatic carboxylic acids include benzoic acid and toluene carboxylic acid. Also

carboxylic diacids can be used, such as for example adipic acid and phthalic acid.

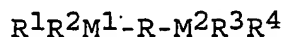
Examples of amine compounds that can be used in the process according to the invention are ammonia and primary and secondary amines. Suitable amine compounds include for example primary aliphatic amines, such as methylamine, ethylamine, butylamine, dodecylamine and the like; primary aromatic amines, such as aniline, toluidine, benzylamine and the like; secondary amines such as dimethylamine, diethylamine, N-methylaniline, dicyclohexylamine, methylhexylamine, and the like; as well as polyamine such as phenylenediamine, ethylenediamine; and heterocyclic amines, such as piperidine.

The telomerization reaction is carried out in the presence of a specific catalyst.

The group VIII metal is preferably chosen from the metals rhodium, nickel, palladium and platinum. Of these, palladium and platinum are preferred. Palladium is most preferred.

Examples of suitable metal sources are metallic platinum or palladium and platinum or palladium on a carrier. Other suitable sources include platinum or palladium cation complexes which are converted into Pd (0) or Pt (0) during the reaction. Examples of such platinum or palladium cation complexes include carboxylates of platinum or palladium. A preferred source of palladium is tetrakis(dibenzylacetone) palladium.

The bidentate ligand has the general formula I



(I)

wherein M^1 and M^2 are independently P, As or Sb;

R¹, R², R³ and R⁴ independently represent a monovalent aliphatic group;

or R¹, R² and M¹ together and/or R³, R⁴ and M² together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M¹ or M² atom, respectively; and R represents a bivalent organic bridging group.

In the bidentate ligand of formula I, M¹ and M² are preferably the same and more preferably they both represent phosphorus atoms.

The bivalent organic bridging group R preferably has from 1 to 6 and more preferably from 2 to 6 atoms in the bridge. By "in the bridge" as used herein is understood to mean the shortest connection between the atoms M¹ and M².

Suitable bridging groups include substituted and unsubstituted alkylene groups. The alkylene group can contain one or more hetero-atoms, such as Si, N, O, S, in the bridge, but preferably has only carbon atoms in the bridge. The alkylene group can be substituted with one or more groups, and is preferably substituted with two groups. The substituents can contain one or more hetero-atoms. Examples of unsubstituted alkylene bridging groups include methylene, ethylene and tri-methylene groups. Examples of substituted alkylene bridging groups include for example 2,2-dimethyl-trimethylene (i.e. neopentylene); 2,2-diethyl-trimethylene, 2,2-dimethyl-tetramethylene, 2-methyl,2-hydroxymethyl-trimethylene (i.e. neopentylol), 2,2 di-hydroxymethyl-trimethylene (i.e. neopentyldiol). Preferred alkylene bridging groups are ethylene, trimethylene and neopentylene groups, preferably connecting respectively the M¹ and M² atom by

the first and the second or the third carbon atom, such as a 1,2-ethylene, a 1,3-trimethylene or a 1,3-neopentylene group. Of these, neopentylene groups are especially preferred. Preferably the neopentylene bridging group is substituted with one or more hydroxy groups.

The bridging group can also comprise one or more aliphatic or aromatic ring structures. Preferably such a bridging group still contains only from 2 to 6 carbon atoms in the bridge. An especially preferred bridging group contains two aromatic ring structures, preferably two benzene rings. These aromatic ring structures are preferably connected to each other and to two alkylene groups which in their turn are connected to respectively M^1 and M^2 .

The alkylene groups are preferably connected to the aromatic ring structures at their ortho positions vis-à-vis the carbon atoms through which the aromatic ring structures are connected.

In a preferred embodiment R^1 , R^2 , R^3 and R^4 independently represent a primary, secondary or tertiary alkyl group. Preferably the alkyl group has from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms. Examples of such alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, iso-butyl, tert-butyl, pentyl, sec-pentyl, cyclopentyl, hexyl, cyclohexyl. Preferably R^1 , R^2 , R^3 and R^4 independently represent a primary alkyl group. Examples of suitable primary alkyl groups include methyl, ethyl and propyl. Preferably the groups R^1 to R^4 represent the same primary alkyl groups, most preferably R^1 to R^4 are methyl or ethyl groups.

In a further preferred embodiment R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively.

By "a cyclic group" is understood a monocyclic or a polycyclic group such as bicyclic or tricyclic groups. Preferred cyclic groups are bicyclic groups. The cyclic group contains at least one hetero-atom, i.e. the M^1 or M^2 atom, respectively, but can contain more hetero-atoms. Suitable hetero-atoms that can further be present in the cyclic group include P, As, Sb, O, N, S and Si. The optionally substituted aliphatic cyclic group contains at least 5 ring atoms. Preferably the cyclic group contains from 6 to 20 ring atoms, more preferably from 6 to 12 ring atoms.

Preferably M^1 and M^2 are both phosphorus and R^1 , R^2 and M^1 together and R^3 , R^4 and M^2 together both represent a phosphabicycloalkyl group. In a highly preferred embodiment the aliphatic cyclic group contains 9 ring atoms and forms a 9-phosphabicyclononyl group. The 9-phosphabicyclononyl group can have several isomeric structures. For the purpose of the invention the [3,3,1] and [4,2,1] isomers are preferred. R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together can both have the same or each have a different isomeric structure. Preferably both R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together have the [3,3,1] structure.

One or both of the phosphabicycloalkyl rings can be substituted with one or more suitable hydrocarbyl groups containing carbon atoms and/or hetero-atoms. Suitable

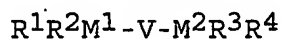
substituents include groups containing hetero-atoms such as halides, sulphur, phosphorus, oxygen and nitrogen. Examples of such groups include chloride, bromide, iodide, thiol, and groups of the general formula $-Y^1-OH$, $-Y^1-CO-OH$, $-Y^1-SH$, $-S-Y^1$, $-O-Y^1$, $-CO-Y^1$, $-NH_2$, $-NHY^1$, $-NY^1Y^2$, $-CO-NY^1Y^2$, $-OH$, $-PO_4$, $-NO_2$, $-NOH$, $-CO$, $-SO_2$, $-S-OH$, in which Y^1 and Y^2 , independently, represent C_1-C_{10} alkyl groups. If a phosphabicycloalkyl ring is substituted it is preferably substituted with a carbon containing group. Such a carbon containing group can, however, contain additional hetero-atoms, such as halides, sulphur, oxygen and nitrogen or hetero-groups as described hereinbefore. Preferably, substituted phosphabicycloalkyl rings are substituted with alkyl groups, preferably having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Linear, branched or cyclic alkyl groups can be used. Suitable alkyl groups include, methyl, ethyl, propyl, iso-propyl, butyl and iso-butyl. More suitably methyl groups are used. If the phosphabicycloalkyl ring is substituted, it can be mono- or poly-substituted and is preferably di-substituted. More preferably the phosphabicycloalkyl ring in this case is substituted with two methyl groups. The phosphabicycloalkyl ring can be substituted at all carbon atoms of the ring. However, the use of rings with substituents on certain carbon atoms can be more beneficial. Suitably, phosphabicyclononyl rings are used with substituents on two carbon atoms, suitably carbon atom 1, 2, 8 and carbon atom 4, 5 or 6.

Examples of preferred bidentate ligands include
1,3-bis(diethylphosphino)-propane;
1,3-bis(dimethylphosphino)-propane;

1,3-bis-(1,4-cyclooctylene-phosphino)-propane, i.e.
 1,3-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-propane;
 1,3-bis-(1,5-cyclooctylene-phosphino)-propane, i.e.
 1,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-propane;
 1,2-bis-(1,4-cyclooctylene-phosphino)-ethane, i.e.
 1,2-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-ethane;
 1,2-bis-(1,5-cyclooctylene-phosphino)-ethane, i.e.
 1,2-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-ethane;
 2,2-dimethyl, 1,3-PP'bis(9-phosphabicyclo-
 [3,3,1]nonyl)-propane;
 2-methyl, 2-hydroxymethyl, 1,3-PP'bis(9-phospha-
 bicyclo[3,3,1]nonyl)-propane;
 2,2-dimethyl, 1,3-PP'bis(9-phosphabicyclo-
 [4,2,1]nonyl)-propane;
 2-methyl, 2-hydroxymethyl, 1,3-PP'bis(9-phospha-
 bicyclo[4,2,1]nonyl)-propane;
 2,2'-bis-(1,4-cyclooctylene-phosphino-methyl)-1,1'-
 biphenyl;
 2,2'-bis-(1,5-cyclooctylene-phosphino-methyl)-1,1'-
 biphenyl;
 and mixtures thereof.

Some of the bidentate ligands that can be used in the present invention are considered to be novel.

The present invention therefore also relates to a bidentate ligand of formula II,



(II)

wherein M^1 and M^2 are independently P, As or Sb;

R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group;

or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted

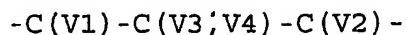
aliphatic cyclic group with at least 5 ring atoms, of which one is the M¹ or M² atom, respectively; and V represents a bridging group comprising a trimethylene group connecting M¹ or M² of which the middle carbon atom has two additional bondings with a non-hydrogen atom.

R¹, R², M¹, M², R³ and R⁴ represent the same groups as described hereinbefore. Preferences are as described hereinbefore.

V represents a bridging group comprising a trimethylene group connecting M¹ or M² of which the middle carbon atom has two additional bondings with a non-hydrogen atom. The middle carbon atom can have two additional bondings with one non-hydrogen atom, i.e. a double bond, or it can have two additional bondings with two separate non-hydrogen atoms.

Examples of non-hydrogen atoms to which the middle carbon group can be double bonded include hetero-atoms, such as oxygen, nitrogen, sulphur or silicon. Furthermore the middle carbon atom can be double bonded to another carbon atom.

Preferably, however, the middle carbon has two additional bondings with two separate non-hydrogen atoms. In a preferred embodiment the bridging group V represents a group having the formula



(IV)

wherein V1 and V2 independently represent an optionally substituted alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl and isopropyl, or hydrogen; and V3 and V4 independently represent a non-hydrogen group.

V3 and V4 each can represent a separate group, or V3, V4 and the middle carbon atom together can form a cyclic group.

If V3, V4 and the middle carbon atom together form a cyclic group, the cyclic group preferably comprises from 3 to 10 ring atoms, more preferably from 3 to 6 ring atoms. The ring atoms can be hetero-atoms or carbon atoms but are preferably carbon atoms.

Preferably, however, V3 and V4 each independently represent a separate hydrocarbyl group containing carbon atoms and/or hetero-atoms. Suitable hydrocarbyl groups for this purpose include groups containing hetero-atoms such as sulphur, phosphorus, oxygen and nitrogen. Examples of such groups include groups of the general formula $-X^1-OH$, $-X^1-CO-OH$, $-X^1-SH$, $-S-X^1$, $-O-X^1$, $-CO-X^1$, $-NH_2$, $-NHX^1$, $-NX^1X^2$, $-CO-NX^1X^2$, $-OH$, $-PO_4$, $-NO_2$, $-NOH$, $-CO$, $-SO_2$, $-S-OH$, in which X^1 and X^2 , independently, represent alkyl or alkylene groups having from 1 to 10 carbon atoms. Preferably V3 and/or V4 represent a carbon containing group. Such a carbon containing group can, however, contain additional hetero-atoms such as halides, sulphur, oxygen and nitrogen or hetero groups as described hereinbefore. Preferably V3 and/or V4 represent groups chosen from methyl, ethyl, propyl, hydroxymethyl and hydroxyethyl.

Preferred bidentate diphosphines according to formula II include
2,2-dimethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane;
2-methyl-2-hydroxymethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane;

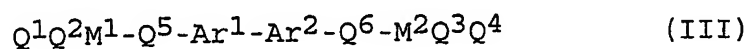
2,2 dihydroxymethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane;
 2,2-dimethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane;
 2-methyl-2-hydroxymethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane;
 2,2 dihydroxymethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane.

These ligands can be prepared by:

- i) reacting P-cyclo-octylene hydride (phosphabicyclic-nonane hydride) and butyllithium to generate a lithium cyclo-octylene phosphide (lithiated phosphabicyclic-nonane).
- ii) introducing a tosylate group to 3-methyl-3-oxetane methanol by reaction with p-toluene sulfonyl chloride in dichloromethane as solvent at 0 °C in the presence of pyridine.
- iii) reacting the phosphide of step i) with the tosylate substituted oxetane of step ii), at for example 0 °C for the first phosphide group and reflux conditions for the second phosphide group, in for example tetrahydrofuran as a solvent.

An illustration of this reaction is given in Figure 1.

The present invention further relates to a bidentate ligand of formula (III),



wherein M^1 and M^2 are independently P, As or Sb;
 Q^1 , Q^2 and M^1 together and Q^3 , Q^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively;

Q^5 and Q^6 each independently represent optionally substituted alkylene groups;

and Ar^1 and Ar^2 independently represent an optionally substituted aromatic group. Bidentate diphosphine ligands having a dimethylenebiphenyl bridge are known in the art.

WO-A-8707600 describes bidentate diphosphines having a dimethylene biphenyl bridge and being substituted at each phosphorus atom with two additional groups.

WO-A-8707600, however, does not disclose any bidentate diphosphine where the phosphorus atom is part of an aliphatic cyclic group.

M^1 and M^2 represent the same groups as described hereinbefore. Preferences are as described hereinbefore.

Q^1 , Q^2 and M^1 together and Q^3 , Q^4 and M^2 together independently represent an optionally substituted cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively. Preferences are the same as for the cyclic groups represented by R^1 , R^2 and M^1 together, and R^3 , R^4 and M^2 together, respectively as described hereinbefore.

Q^5 and Q^6 each independently represent an optionally substituted alkylene group. Preferably this alkylene group contains from 1 to 6, more preferably from 1 to 4 carbon atoms. The alkylene group can be substituted with one or more hydrocarbyl groups. If the alkylene group is substituted, it is preferably substituted with alkyl groups, preferably having from 1 to 6, more preferably from 1 to 4 carbon atoms.

Preferably the alkylene group is unsubstituted. Preferably both alkylene groups are the same and preferably both alkylene groups are unsubstituted.

methylene or ethylene groups. Most preferably both Q⁵ and Q⁶ represent an unsubstituted methylene group.

Ar¹ and Ar² each independently represent an aromatic group. Preferably the aromatic group contains from 6 to 20 carbon atoms, more preferably from 6 to 14 carbon atoms. Examples of suitable aromatic groups include phenyl, naphthyl, phenanthryl and anthracenyl. Of these, phenyl groups are preferred. The aromatic group can be substituted with one or more hetero-atoms and/or hydrocarbyl groups. Hydrocarbyl groups used for this purpose include alkyl, alkoxy and carbonyl groups. Preferably the aromatic group is unsubstituted. The aromatic groups are preferably connected with each other by the carbon atom next to the carbon atom attached to the alkylene group.

Preferred bidentate diphosphine according to formula III include

2,2'-bis-(1,4-cyclooctylene-phosphino-methyl)-1,1'-biphenyl;

2,2'-bis-(1,5-cyclooctylene-phosphino-methyl)-1,1'-biphenyl, and mixtures thereof.

These ligands can be prepared by reacting P-cyclooctylene hydride (phosphabicyclononane hydride) and butyllithium to generate a lithium cyclo-octylene phosphide (lithiated phosphabicyclononane). The latter phosphide is reacted with a 2,2'-dimethyl-1,1'-biphenyl group substituted with suitable leaving groups, preferably tosylates, mesylates and triflates, in an appropriate manner. Preferred aliphatic groups are those having a cyclic sulphate structure as a leaving group, such as cyclic substituted or unsubstituted alkane diol sulphate esters, also called cyclic alkyl sulphates.

For example 2,2'-bis-(1,4-cyclooctylene-phosphino-methyl)-1,1'-biphenyl can be prepared by reacting phosphabicyclononane hydride and butyllithium to generate the corresponding lithium phosphide and subsequently reacting this lithium phosphide, at for example 0 ° C in tetrahydrofuran, with the di-p-tosylate ester of 2,2'-dimethyl-1,1'-biphenyl wherein the tosylate groups are substituted on the methyl groups.

The P-cyclo-octylene hydride (phosphabicyclononane hydride) may conveniently be prepared as described by Elsner et al. (Chem. Abstr. 1978, vol. 89, 180154x).

The present invention further provides a catalyst system comprising:

- I) a source of group VIII metal;
- II) a bidentate ligand according to the general formula II or III as described hereinbefore.

The catalyst system according to this invention can be advantageously used for the telomerization of conjugated dienes.

The amount of telomerization catalyst to be used is not critical, and any catalytically effective amount may be used. In general, amounts between 0.000001 and 1, and preferably between 0.000005 and 0.01 gram atom of Group VIII metal per mole of conjugated diene can be used. In order to achieve high catalyst efficiencies without having to recycle the catalyst, amounts of less than 0.0001, preferably less than 0.00005, and more preferably less than 0.00002 gram atoms of Group VIII metal are used per mole of conjugated diene.

The bidentate ligand is generally used in a relative amount of from 1 to 20 moles, and preferably from 2 to 15 moles of bidentate ligand per gram atom of the Group VIII metal. The bidentate ligand can be added as a separate

compound to the reaction mixture or zone or to a catalyst make-up solution, or it may be incorporated in a Group VIII metal complex.

The process according to the present invention should preferably be conducted in the substantial absence of oxygen, as oxygen reacts with the bidentate ligand and consequently may result in decreased catalyst activity.

In the process of the invention, one or more of the reactants and/or the formed product may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the carbonylation reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes are recommended. Further suitable solvents include ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole, and ketones, such as methylbutylketone. Solvents, comprising or substantially consisting of sulphones are also preferred. Sulphones are in particular preferred, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), sulfolane, 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

The temperature at which the telomerization reaction is carried out is not critical. Normally, temperatures between ambient temperature and 150 °C can be used. Preferably, the reaction temperature is from 40 to 100°C and more preferably from 50 to 100 °C.

The pressure at which the telomerization reaction is carried out is not critical. Generally the reaction pressure lies between 1 and 10 bars.

The telomerization reaction can be carried out continuously, semi-batch or batch-wise.

The invention will be illustrated by the following non-limiting examples.

Examples 1-9 and comparative example A

The experiments were carried out in a 250 ml Hastelloy C autoclave. The telomerization catalyst was prepared separately as a 5 ml methanol solution of 0.25 mmol Pd(dibenzylacetone)₂ and 0.3 mmol bidentate ligand as given in Table I. The catalyst solution was introduced under a nitrogen atmosphere to a medium of alkanol and optionally additional inert solvent in the autoclave as indicated in Table I. The autoclave was closed, evacuated and 15 ml 1,3 butadiene was pumped in.

Subsequently, the reactor was sealed and the contents were heated to a temperature as specified in Table I. The temperature was maintained during the reaction time as specified in Table I. Thereafter the autoclave was cooled to room temperature and the contents were analyzed by standard GLC. The obtained reaction rate and selectivity towards the linear 1-substituted 2,7-octadiene are given in Table I. Generated by-products included vinylcyclohexene and mono-butenyl ethers.

The mono-butenyl ethers can be very useful in a wide range of other applications. The reaction rate is defined as the average rate over 90% butadiene conversion.

Table I

Example	Medium	Bidentate ligand	Temperature	Reaction time (hours)	Reaction rate (mol/mol/hr)	Selectivity towards linear telomerization product
1	20 ml methanol/ 40 ml diglyme	BDEPP	70	0.5	1400	91.5
2	20 ml methanol/ 40 ml NMP	BDEPP	70	0.5	1000	90
3	20 ml methanol/ 40 ml diglyme	BDMPP	70	0.25	2000	94
4	20 ml methanol/ 40 ml diglyme	BCOPP	70	1.5	500	93
5	50 ml methanol	MHBCOPP	70	0.25	3000	95
6	50 ml methanol	BCOPE	70	0.25	2000	94
7	50 g phenol/ 40 ml diglyme	BCOPE	60	0.5	1500	90

Table I continued

Example	Medium	Bidentate ligand	Temperature	Reaction time (hours)	Reaction rate (mol/mol/hr)	Selectivity towards linear telomerization product
8	50 ml methanol	1,4 BCOPMB	70 increased to 85	n.d.	n.d.	961
9	50 ml methanol	1,5 BCOPMB	70	n.d.	n.d.	922
A	50 ml methanol	DPPP	70	5	n.d.	3

n.d. = not determined

BDEPP = 1,3-bis(diethylphosphino)-propane

BDMPP = 1,3-bis(dimethylphosphino)-propane

BCOPP = mixture of 1,3-bis (1,4-cyclo-octylenephosphino) propane and 1,3-bis(1,5-cyclo-octylenephosphino) propane

BCOPE = mixture of 1,2-bis (1,4-cyclo-octylenephosphino) ethane and 1,2-bis(1,5-cyclo-octylenephosphino) ethane

MHBCOPP = 2-methyl, 2-hydroxymethyl, 1,3-bis (1,4-cyclo-octylenephosphino) propane

1,4 BCOPMB = 2,2'-bis-(1,4-cyclooctylene-phosphino-methyl)-1,1'-biphenyl

1,5 BCOPMB = 2,2'-bis-(1,5-cyclooctylene-phosphino-methyl)-1,1'-biphenyl

NMP = N-methyl-2-pyrrolidone

DPPP = 1,3-bis(diphenylphosphino)-propane

1 = only 4% telomerization product was formed, whereas 59% mono-butenyl ethers were formed

2 = only 31% telomerization product was formed, whereas 59% mono-butenyl ethers were formed

3 = only traces of ethers were formed

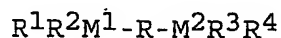
C L A I M S

1. Process for the telomerization of a conjugated diene,

wherein the conjugated diene is reacted with a compound containing an active hydrogen atom and having a formula R-H in the presence of a telomerization catalyst based on:

- (a) a source of group VIII metal,
- (b) a bidentate ligand

wherein the bidentate ligand has the general formula I



(I)

wherein M^1 and M^2 are independently P, As or Sb;
 R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group;

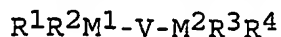
or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively;

and R represents a bivalent organic bridging group.

2. Process according to claim 1, wherein the conjugated diene is 1,3-butadiene.

3. Process according to claim 1 or 2, wherein the active hydrogen-containing compound is water, an alkanol or an hydroxy-aromatic compound.

4. Bidentate ligand of formula II,



(II)

wherein M^1 and M^2 are independently P, As or Sb;

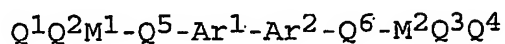
R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group;

or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively;

and V represents a bridging group comprising a trimethylene group connecting M^1 or M^2 of which the middle carbon atom has two additional bondings with a non-hydrogen atom.

5. Bidentate ligand according to claim 4, wherein the bidentate ligand is chosen from 2,2-dimethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane, 2-methyl-2-hydroxymethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane or 2,2 dihydroxymethyl-1,3-bis-(1,4-cyclooctylene-phosphino)-propane; 2,2-dimethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane, 2-methyl-2-hydroxymethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane or 2,2 dihydroxymethyl-1,3-bis-(1,5-cyclooctylene-phosphino)-propane.

6. Bidentate ligand of formula (III);



(III)

wherein M^1 and M^2 are independently P, As or Sb;

Q^1 , Q^2 and M^1 together and Q^3 , Q^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively;

Q^5 and Q^6 each independently represent optionally substituted alkylene groups;

and Ar¹ and Ar² independently represent an optionally substituted aromatic group.

7. Bidentate ligand according to claim 6, wherein the bidentate ligand is 2,2'-bis-(1,4-cyclooctylene-phosphino-methyl)-1,1'-biphenyl or 2,2'-bis-(1,5-cyclooctylene-phosphino-methyl)-1,1'-biphenyl.

8. Catalyst system comprising

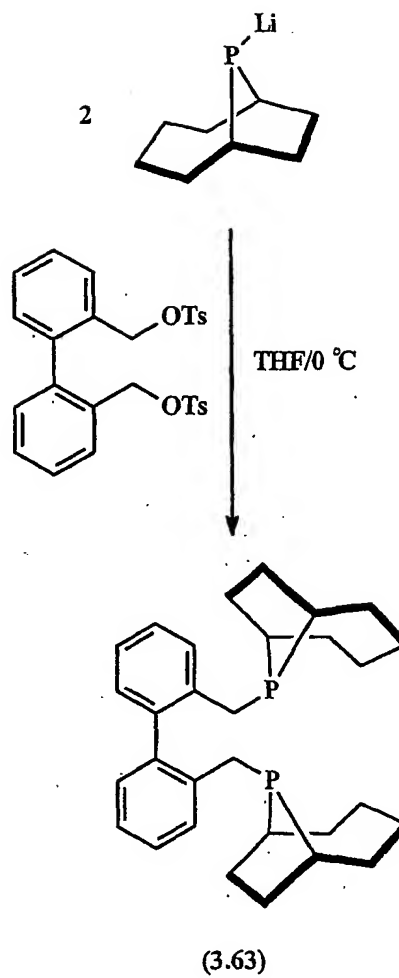
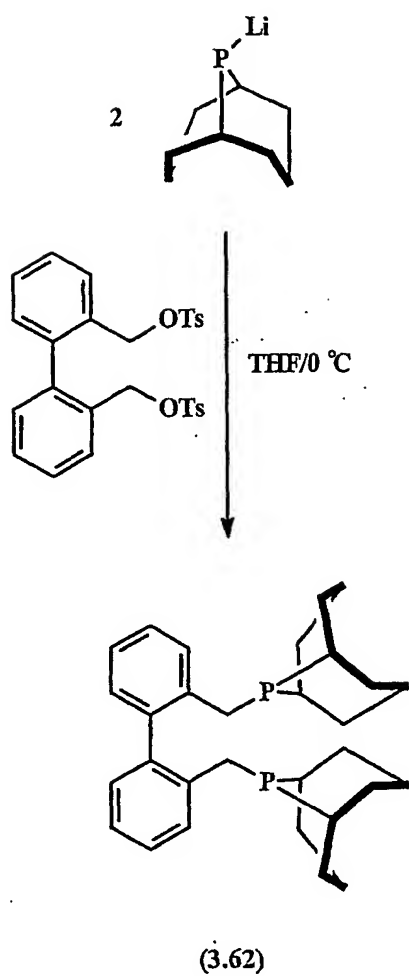
- I) a source of group VIII metal;
- II) a bidentate ligand according to any one of claims 4 to 7.

9. Process according to claim 1, carried out in the presence of a catalyst according to claim 8.

10. Process for the preparation of 1-octene, comprising:

- a) telomerization of 1,3-butadiene according to any one of claims 1-3 or 9 to form 1-substituted-2,7-octadiene;
- b) hydrogenation of the 1-substituted-2,7-octadiene of step a) to form 1-substituted octane;
- c) decomposing the 1-substituted octane of step b) to form 1-octene.

Figure 1:



(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 2003/040065 A3

(51) International Patent Classification⁷: **C07B 37/02**,
C07C 41/06, B01J 31/24, C07F 9/50, 9/6568

Amsterdam (NL). PRINGLE, Paul, Gerard [GB/GB];
Cantocks Close, Bristol, Avon BS8 1TS (GB).

(21) International Application Number:
PCT/EP2002/012381

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
5 November 2002 (05.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:
60/348,205 9 November 2001 (09.11.2001) US

(71) Applicant (*for all designated States except US*): SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

Published:
— with international search report

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): DRENT, Eit
[NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).
EBERHARD, Michael, Rolf [DE/US]; 2545 McCarthy
Mall, Honolulu, HI 96822 (US). VAN DER MADE,
Renata, Helena [NL/NL]; Badhuisweg 3, NL-1031 CM

(88) Date of publication of the international search report:
22 January 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BIDENTATE LIGAND FOR THE TELOMERIZATION OF DIENES

(57) Abstract: Process for the telomerization of a conjugated diene, wherein the conjugated diene is reacted with a compound containing an active hydrogen atom and having a formula R-H in the presence of a telomerization catalyst based on: (a) a source of group VIII metal, (b) a bidentate ligand wherein the bidentate ligand has the general Formula (I): $R^1R^2M^1-R-M^2R^3R^4$ wherein M^1 and M^2 are independently P, As or Sb; R^1 , R^2 , R^3 and R^4 independently represent a monovalent aliphatic group; or R^1 , R^2 and M^1 together and/or R^3 , R^4 and M^2 together independently represent an optionally substituted aliphatic cyclic group with at least 5 ring atoms, of which one is the M^1 or M^2 atom, respectively; R represents a bivalent organic bridging group; and novel bidentate diphosphines which can be used in this process.

WO 2003/040065 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/12381

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07B37/02 C07C41/06 B01J31/24 C07F9/50 C07F9/6568

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07B C07C B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)
CHEM ABS Data, EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 96, no. 25, 21 June 1982 (1982-06-21) Columbus, Ohio, US; abstract no. 217253, KURARAY CO., LTD., JAPAN: "Telomerization of butadiene and isoprene" XP002244618 abstract & JP 57 007426 A (KURARAY CO., LTD., JAPAN) 14 January 1982 (1982-01-14)	1,2
A	WO 92 10450 A (DOW BENELUX N.V.) 25 June 1992 (1992-06-25) cited in the application page 8 --- -/-	1-3,8-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 June 2003

Date of mailing of the international search report

07/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Beslier, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12381

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 311 352 A (AMERSHAM INTERNATIONAL) 12 April 1989 (1989-04-12) claims 6,7 ---	4
X	WO 91 03262 A (AMERSHAM INTERNATIONAL) 21 March 1991 (1991-03-21) page 39 ---	4
X	KARSCH H.H. ET AL.: "Funktionelle Trimethylphosphanderivate, XVIII (1). Methyl(phosphinomethyl)silane und -stannane." ZEITSCHRIFT FUR NATURFORSCHUNG, TEIL B: ANORGANISCHE CHEMIE, ORGANISCHE CHEMIE., vol. 38b, no. 11, 1983, pages 1399-1405, XP008018568 VERLAG DER ZEITSCHRIFT FUR NATURFORSCHUNG. TUBINGEN., DE ISSN: 0932-0776 compound of formula 6b ---	4
X	MORIMOTO, T. ET AL: "A convenient method for the synthesis of bis(trialkylphos- phine)-boranes bearing two phospholanes" SYNLETT (1996), (12), 1211-1212 , 1996, XP002244948 the whole document ---	6
A	WO 00 09521 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 24 February 2000 (2000-02-24) examples 4,8 ---	6
A	WO 00 56695 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 28 September 2000 (2000-09-28) example 5 -----	6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/12381

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 57007426	A	14-01-1982	JP 1006175 B JP 1522610 C	02-02-1989 12-10-1989
WO 9210450	A	25-06-1992	CA 2097297 A1 WO 9210450 A1 DE 69020586 D1 DE 69020586 T2 EP 0561779 A1 ES 2074256 T3 JP 6506189 T	14-06-1992 25-06-1992 03-08-1995 11-04-1996 29-09-1993 01-09-1995 14-07-1994
EP 311352	A	12-04-1989	AT 63559 T CA 1336438 C DE 3862843 D1 DK 171487 B1 EP 0311352 A1 ES 2037234 T3 WO 8903388 A1 IL 87944 A JP 1128990 A JP 2002706 C JP 7037472 B KR 9711165 B1 US 4916214 A	15-06-1991 25-07-1995 20-06-1991 25-11-1996 12-04-1989 16-06-1993 20-04-1989 31-07-1994 22-05-1989 20-12-1995 26-04-1995 08-07-1997 10-04-1990
WO 9103262	A	21-03-1991	AT 131072 T CA 2039732 A1 DE 69024038 D1 EP 0441953 A1 WO 9103262 A1 JP 4506810 T JP 3221875 B2 JP 3341001 B2 JP 2002060397 A US 5589576 A US 6124440 A US 6329513 B1 US 6001979 A US 2002082398 A1	15-12-1995 01-03-1991 18-01-1996 21-08-1991 21-03-1991 26-11-1992 22-10-2001 05-11-2002 26-02-2002 31-12-1996 26-09-2000 11-12-2001 14-12-1999 27-06-2002
WO 0009521	A	24-02-2000	AU 5852299 A WO 0009521 A1	06-03-2000 24-02-2000
WO 0056695	A	28-09-2000	AU 756055 B2 AU 3290700 A BR 0009187 A CA 2367935 A1 CN 1344242 T WO 0056695 A1 EP 1163202 A1 JP 2002540091 T	02-01-2003 09-10-2000 26-12-2001 28-09-2000 10-04-2002 28-09-2000 19-12-2001 26-11-2002

THIS PAGE BLANK (USPTO)